PHOTOINDUCED ABSORPTION SPECTRA IN AMORPHOUS Si:H and Ge:H AND MICROCRYSTALLINE Si:H

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ABSTRACT

The steady state subgap photoinduced absorpotion bands in a-Ge:H and a-Si:H are interpreted in terms of two kinds of optical transitions of photoexcited carriers from traps in the gap into the bands of which one produces absorption and the other produces bleaching. The photoinduced absorption in microcrystalline Si:H is due to free carriers in the crystalline grains whose recombination is dominated by the surrounding amorphous matrix.

INTRODUCTION

We have applied the steady state (ss) photoinduced absorption technique to hydrogenated a-Si, a-Ge and microcrystalline (μc) silicon. We show that the PA bands observed in both a-Si:H and a-Ge:H can be interpreted in terms of photoionization of trapped carriers, provided a bleaching process is added that sharpens the high energy side of the spectrum and makes the spectrum more symmetrical. We show that the inclusion of the bleaching process provides a unique opportunity to determine the effective electron correlation energy in the localized state involved in the induced optical transitions. The PA spectrum in the μc-Si:H samples is very different: the absorption increases monotonously with increasing wavelength. We interpret it as due to free carrier absorption which occurs in the crystalline grains. The temperature and pump intensity dependences indicate that the recombination in μc materials is governed by the amorphous matrix.

EXPERIMENTAL

The experimental set-up for the ss PA is described elsewhere[1]. For excitation (pump) we used a CW Ar^+ laser at 2.4 eV, chopped at 150 Hz. The variable wavelength probe beam was an incandescent light source (glow-bar or tungsten lamp) followed by a monochromator. The probe beam transmission (T) and its photoinduced changes (ΔT) were measured with detectors (Si, PbS or PbSe) and a lock-in amplifier. The system response was accounted for by calculating the ratio $\Delta T/T$ which is proportional to the change $\Delta\alpha$ of the absorption coefficient α. The samples were held in an open-cycle cryostat and measurements were taken from 10 to 300 K.

All our samples were thin films prepared by the glow-discharge process. The a-Si:H films were prepared at Exxon

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Research (Linden) and the a-Ge:H sample was prepared at IBM (San Jose). The μc samples were made at Nanjing University; different grain sizes were obtained by varying the rf power from 13 to 145 W, while keeping the substrate temperature at 300°C. The substrates were either fused silica or crystalline Si.

PA SPECTRA in a-Ge:H and a-Si:H

The PA spectra of a-Ge:H and a-Si:H are shown in Figs. 1 and 2. The dominant feature is the subgap PA band which is sharper in a-Ge:H. The spectrum of the PA band and its strength do not change much with temperature in a-Ge:H while in a-Si:H the spectrum shifts to higher energies and its strength decreases as the temperature increases[1]. The additional absorption at high energies which is stronger at high temperatures is associated with the temperature modulation of the energy gap[2] and will not be discussed in this work.

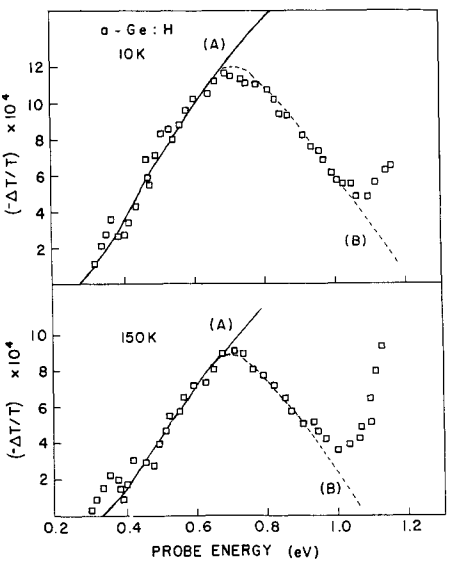

Fig. 1: PA spectra in a-Ge:H at 10 and 150 K. The theoretical curves are based on the ITO model. Curve A absorption only, curve B includes the contribution of the bleaching process.

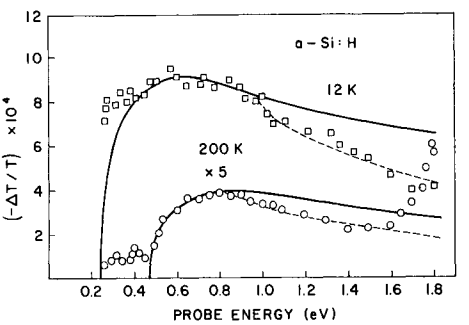

Fig. 2: PA in a-Si:H at 12 and 200K. Curves A and B are theoretical fits as in Fig. 1 but using the OT model.

The PA band in a-Si:H has been ascribed to photoionization of holes trapped in the tail of the valence band into the valence band[1,3]. These transitions are schematically shown in Fig. 3(a) with an onset t_1. If the distribution of tail states (DOS) is sufficiently sharp, most photoexcited holes are concentrated in a

narrow energy interval around the quasi-Fermi level F_p. Assuming that the optical matrix elements are independent of energy (O'Connor-Tauc model[4] - OT) and the DOS in the valence band is proportional to $(E_v-E)^{\frac{1}{2}}$, $\Delta\alpha$ near the onset of the PA band is

$$\Delta\alpha = N_{ss}B(\hbar\omega - E_o)^{\frac{1}{2}}/\hbar\omega \qquad (1)$$

where the threshold $E_o = F_p - E_v$ (Fig. 3(a)), N_{ss} is the ss carrier density and B is a constant[4].

A slightly different equation for $\Delta\alpha$ can be deduced in a similar way as Eq. (1), if the DOS above E_v is not sharp in the region of F_p. Assuming the DOS to be constant near F_p, the initial states can be integrated in Eq. (1) to yield[2]

$$\Delta\alpha = N_{ss}C(\hbar\omega - E_o)^{3/2}/\hbar\omega \qquad (2)$$

where C is a constant. We refer to this model as integrated O'Connor-Tauc model (IOT).

These formulas fit reasonably well the onsets of the PA bands in a-Si:H and in a-Ge:H as shown in Figs. 1, 2 (curves A). For well prepared a-Si:H films, Eq. (1) was shown to fit the PA onset data at all temperatures[1,4]. For a-Ge:H and not so well prepared a-Si:H films with a higher DOS in the gap, Eq. (2) fits better the PA onsets. None of the proposed equations can account for the PA band decay at high energies as seen in Figs. 1 and 2. This discrepancy could be removed by making suitable assumptions about the optical matrix elements which depend on the wavefunction of the trapping state, as was recently proposed by Hirabayashi and Morigaki[5] for a-Si:H. However these choices are arbitrary unless they can be justified on theoretical grounds. Instead, we have recently proposed[2] a straight-forward explanation to account for the systematic deviations at high energies from the curves expressed by Eqs. (1) and (2) (Figs. 1,2). This explanation is based on considering a bleaching process associated with photoinduced reduction of the optical transitions which contribute to the absorption below the absorption edge.

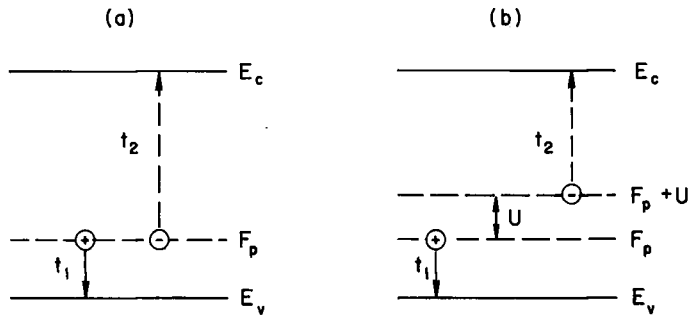

Fig. 3: (a) Schematic representation of the optical transitions onsets: t_1 for absorption, t_2 for bleaching, F_p is the hole quasi-Fermi level. (b) The effective correlation energy U is included.

MODEL FOR PA SPECTRA

In the dark, the valence-band tail is filled with electrons. These electrons produce ordinary absorption associated with their transitions into the conduction band[6] whose onset is represented in Fig. 3(a) by transition t_2. When photoexcited holes are trapped at F_p, the density of initial states of electrons is reduced, therefore transitions into E_c are bleached. If the hole density at F_p is p, the total photoinduced change in α is

$$\Delta\alpha = [\sigma_1(\omega) - \sigma_2(\omega)]p \qquad (3)$$

where $\sigma_1(\omega)$ is the absorption cross-section for hole transitions into the valence band and $\sigma_2(\omega)$ is the absorption corss-section for electron transitions into the conduction band. For their frequency dependencies we have used Eq. (1) (OT model) or Eq. (2) (IOT model). We have obtained good fits to the data in Figs. 1,2 (curve B) using the IOT model for a-Ge:H and the OT model for a-Si:H, applying the same model for absorption (σ_1) and bleaching (σ_2). We note that the ratio C_1/C_2 of the factors C defined in Eq. (2) (where 1 represents absorption and 2 represents bleaching) is 0.6 in a-Ge:H and the ratio B_1/B_2 in Eq. (1) for a-Si:H is 1.5.

As apparent from Fig. 3(a) the threshold energies for absorption E_1 and for bleaching E_2 should satisfy the relation $E_1 + E_2 = E_g$, where E_g is the energy-gap. However, the values E_1, E_2 extracted from the fits in Figs. 1 and 2, do not satisfy this relation[2]. The deviation ΔE, $\Delta E = E_g - (E_1 + E_2)$, in a-Ge:H is of order 0.1 eV, while in a-Si:H ΔE is of order 0.3 eV. This deviation can be explained if electron correlation energy is considered[7].

The states which produce PA are empty under steady state illumination conditions and are concentrated near F_p. The corresponding states in the dark are doubly occupied and therefore have energies close to $F_p + U$, where U is the effective electron correlation energy. This is shown in a one-electron energy diagram[8] in Fig. 3(b) for a positive U. In this case the threshold energies observed in PA satisfy the relation $E_1 + E_2 + U = E_g$ and $\Delta E = U$. This enables us to determine U by PA measurements. We note that U found by ESR[9] for energy levels close to mid-gap is about 0.1 eV in a-Ge:H[10] and about 0.4 eV in a-Si:H[9,10]. These values are in good agreement with ΔE extracted from the fit to the PA data in both materials.

PA in MICROCRYSTALLINE Si:H

The PA spectra for μc-Si:H films are shown in Fig. 4 for sample C (grain size L ≃ 220 Å) and sample E (L ≃ 830 Å). The extra absorption seen in sample C below 0.4 eV dominates the absorption in the whole energy range in sample E. This PA monotonously increases with decreasing $\hbar\omega$. The log-log plot in Fig. 5 shows that the wavelength dependence is a power law, $-\Delta T/T \sim \lambda^{\gamma}$, where γ is between 1.5 to 1.8, similar to that observed

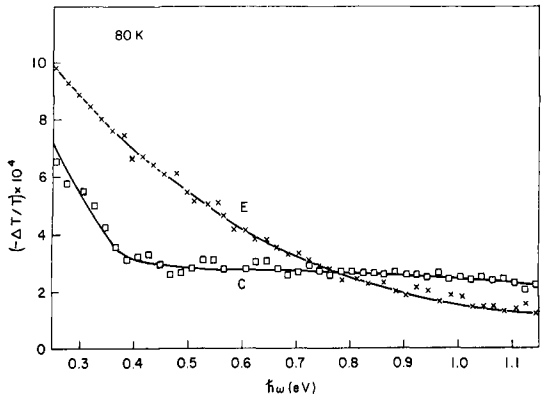

Fig. 4: PA spectra of μc-Si:H with different grain size L. Sample C: L ≃ 220 Å, sample E: L ≃ 830 Å.

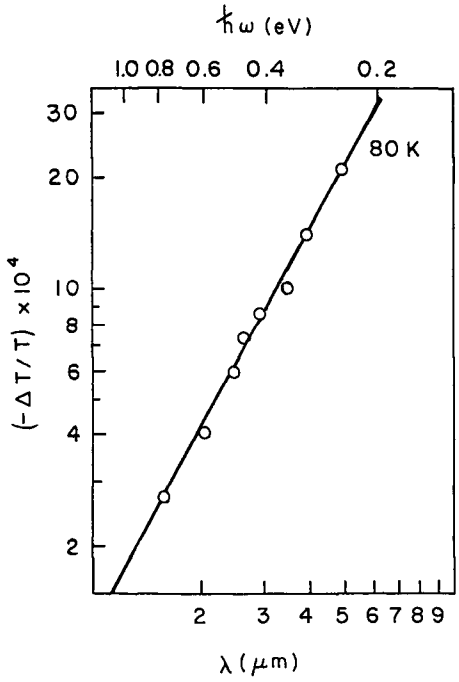

Fig. 5: Wavelength dependence of PA in μc-Si:H, sample E. The slope of the straight line is γ = 1.8.

for free-carrier absorption in crystals[11]. We therefore ascribed these PA spectra to photogenerated free carriers and refer to them as PFA.

Compared to c-Si, PFA in μc-Si:H has a different temperature and pump intensity dependences[12]. In μc-Si:H, PFA decreases with temperature θ as $-\Delta T/T \sim \exp(-\theta/\theta_o)$ where θ_o is a constant (whose value in different samples was between 150 and 270 K), while in c-Si PFA increases with θ following a power law. We have also found that PFA in μc films depends sublinearly on the laser intensity $I(-\Delta T/T \sim I^{\delta}$ where δ was between 0.4 to 0.6). On the contrary, in c-Si PFA increases linearly with I. We also note that PFA is larger in μc-Si:H than in c-Si by about two orders of magnitude.

The dependences of PFA in μc-Si:H on temperature and laser intensity are the same as those found for the PA in good quality a-Si:H samples[1] where they were interpreted as due to recombination involving transport processes dominated by exponential distributions of trap densities below the band edges[3]. It is therefore plausible to assume that the μc-Si:H films have large densities of traps comparable to those in a-Si:H. However, in a-Si:H PFA is not observed[3] because carriers are quickly trapped. We can explain our results in μc-Si:H by a two phase model in which the μc grains are surrounded by an amorphous matrix that is similar to a-Si:H[13]. The PFA occurs in the μc grains while the carrier recombination is dominated by the amorphous matrix.

Generally, PFA $\sim N_{ss}/\tau_{rel}$, where τ_{rel} is the momentum relaxation time (of order 10^{-13} sec in c-Si). It does not seem likely that the much larger PFA in μc-Si:H compared to c-Si is due to a much shorter τ_{rel} in the μc grains. We propose that the main reason is a larger N_{ss} in the grains, associated with a longer recombination time. We assume that a barrier between the grains and the amorphous matrix separates electrons and holes[12] and therefore reduces their recombination rate. Since the PA band, associated with hole trapping in a-Si:H[3], is not observed in μc samples, we must assume that electrons are pushed into the matrix while the holes remain in the grains. The dynamics of electrons in the matrix determines the recombination process as in a-Si:H, and therefore the temperature and intensity dependences are similar.

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